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-78. (New) A method of passivating a multiplayer conductive structure,

comprising:

layering a first conductive material;

introducing a selection of CF4, HCl, and BCl3 gases to the first

conductive material; and

layering a second conductive material over the first conductive

material .--

## **REMARKS**

Claims 43, 44, 76, and 77 along with newly added claim 78 are currently pending in the present application. This amendment is being filed as part of a request for continued examination under 37 C.F.R. § 1.114. In the final Office Action mailed August 28, 2001, the Examiner rejected claims 76 and 77 under the 35 U.S.C. § 102(e) as being anticipated by U.S. Patent No. 6,204,203 B1 to Narwankar *et al.* ("Narwankar"). Claims 43 and 44 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Narwankar.

Applicant's invention exposes a conductive layer to an oxygen-inhibiting plasma or other gas, including nitrogen free gases, prior to the formation of the another layer or layers on the conductive layer to substantially reduce the association of oxygen with the conductive layer during formation of the other layer or layers. By reducing the amount of oxygen associated with the conductive layer, the electrical characteristics of a semiconductor device including the conductive layer are improved, as will be discussed in more detail below with reference to the disclosed embodiments of the invention. In order to help the Examiner appreciate certain distinctions between the pending claims and the subject matter of the applied reference, the disclosed embodiments of the invention will now be discussed in comparison to the applied reference. Specific distinctions between the pending claims and the applied references will be discussed after the discussion of the disclosed embodiments and the applied reference. This

discussion of the differences between the disclosed embodiments and applied reference does not define the scope or interpretation of any of the claims.

One embodiment of the present invention is discussed with reference to Figures 7-10 in which an interposing layer 52 such as a tungsten nitride layer 52 is formed between a conductive plug 46 formed in a via 44 and a conductive line material 48 formed in a trench or container 50. The tungsten nitride layer 52 enhances the electrical contact between the line material and the plug, promotes adhesion of the line material within the container 50, prevents or slows the diffusion of materials across the tungsten nitride layer boundary, or serves some other purpose. As previously described, the tungsten nitride layer 52 may associate with oxygen after it is formed and subsequent thermal processes may result in the formation of an oxide layer 54 between the tungsten nitride layer 52 and the line material 48. Because the oxide layer 54 is an insulator, this layer will adversely affect the electrical connection between the line material 48 and the plug 46. By exposing the tungsten nitride layer 52 to an oxygen-inhibiting agent or a reducing atmosphere prior to formation of the line material 48, the thickness of the oxide layer 54 is reduced to a thickness of less than 10 angstroms or entirely eliminated as illustrated respectively in Figures 9 and 10. Thus, in all embodiments a conductive layer is exposed to an oxygen-inhibiting agent or reducing atmosphere prior to another layer being formed on the conductive layer to thereby reduce an ability of the conductive material to associate with oxygen.

As described in the specification, the tungsten nitride layer 52 or other conductive layer may be treated in a plasma such as an N<sub>2</sub> and H<sub>2</sub> plasma, an NH<sub>3</sub> plasma, or an N<sub>2</sub> plasma. See page 6, lines 13-30 and page 7, lines 1-19. Furthermore, the conductive layer may be treated in a nitrogen-free gas, such as a plasma treatment including H<sub>2</sub> or other gases such as B<sub>2</sub>H<sub>6</sub>, PH<sub>3</sub>, CH<sub>3</sub>SiH<sub>3</sub>, (CH<sub>3</sub>)<sub>3</sub>Si-Si(CH<sub>3</sub>), HMDS, CF<sub>4</sub>, CHF<sub>3</sub>, HCL, BCl<sub>3</sub>, and silane SiH<sub>4</sub>, and any combinations of these gases, as described on page 7, lines25-30, page 8, lines 1-16, and page 9, lines 1-12. As will be appreciated by those skilled in the art, the use of a plasma treatment enables energy of ions forming the plasma to be closely controlled to thereby more precisely treat the tungsten nitride layer as desired. Moreover, the other nitrogen-free gases provide beneficial treatment of the conductive layer when compared to nitriding of the layer by exposure to a nitrogen containing gas and the associated heat treatment.

Another embodiment of the present invention is illustrated in Figures 4 and 5 that depict an in-process semiconductor device. As mentioned in the specification, for the purposes

of explanation the in-process semiconductor device is assumed to be a capacitor in the process of being constructed. In Figure 4, the capacitor includes a first conductive layer or 24, which may be formed from hemispherical silicon grain (HSG), formed over a substrate 22, and a dielectric 26 formed on the first conductive layer. In the examples of Figures 4 and 5, the dielectric 26 is formed from tantalum pentoxide Ta<sub>2</sub>O<sub>5</sub>. A second conductive layer 28 formed from tungsten nitride WN<sub>x</sub> is then formed on the dielectric 26. The tungsten nitride layer 28 has a tendency to associate with oxygen, particularly if that layer is exposed to oxygen prior to a third conductive polysilicon layer 30 being formed on the tungsten nitride layer 28. During subsequent processing of the capacitor, the oxygen contained in the tungsten nitride layer 28 can combine with silicon from the polysilicon layer 30 to form an unwanted silicon dioxide layer 36 between the tungsten nitride layer 28 and the polysilicon layer 30. For example, a thermal process step such as the formation of a borophosphosilicate glass (BPSG) layer 34 over the polysilicon layer 30, which of course occurs after the formation of the polysilicon layer 30, may cause a reaction between the polysilicon layer 30 and the oxygen in the tungsten nitride layer 28 and thereby form the silicon dioxide layer 36.

Ideally, the HSG layer 24 forms a first plate of the capacitor, the tantalum pentoxide 26 forms the dielectric of the capacitor, and the tungsten nitride layer 28 and polysilicon layer 30 form the second plate of the capacitor. With the formation of silicon dioxide layer 36, however, the capacitor now includes a first capacitor corresponding to the HSG layer 24, tantalum pentoxide 26, and tungsten nitride layer 28, and a second capacitor in series with the first capacitor, with the second capacitor corresponding to the tungsten nitride layer 28, silicon dioxide layer 36, and polysilicon layer 30. These first and second capacitors connected in series have a combined capacitance that is less than that of the ideally formed capacitor. As will be understood by those skilled in the art, the thickness of the silicon dioxide layer 36 affects the value of the combined capacitance.

In the capacitor of Figure 4, the thickness of the silicon dioxide layer 36 is greatly reduced by exposing the tungsten nitride layer 28 to an oxygen-inhibiting agent prior to the formation of the polysilicon layer 30 to thereby greatly reduce the association of the tungsten nitride layer with oxygen. The silicon dioxide layer 36 in the embodiment of Figure 4 is less than 10 angstroms thick due to the oxygen-inhibiting agent, while in a conventional capacitor shown in Figure 3 the silicon dioxide layer 36 is about 10-40 angstroms thick. In the capacitor

of Figure 5, the exposure of the tungsten nitride layer 28 to the oxygen-inhibiting agent eliminates the formation of the silicon dioxide layer 36 altogether.

The oxygen-inhibiting agent may be an N<sub>2</sub> and H<sub>2</sub> plasma, with the tungsten nitride layer 28 ideally being exposed to this plasma prior to exposing tungsten nitride layer to an atmosphere associated with the formation of the polysilicon layer 30 or prior to exposing the tungsten nitride layer to oxygen. As described in the specification, it is believed the exposure of the tungsten nitride layer 28 to the N<sub>2</sub> and H<sub>2</sub> plasma or any of the other oxygen-inhibiting agents stuffs the tungsten nitride layer grain boundaries with nitrogen or otherwise passivates the tungsten nitride layer, making the bonds at the grain boundaries less active and less likely to associate with oxygen. It should be noted that even if the tungsten nitride layer 28 is exposed oxygen, the layer may thereafter be exposed to a reducing atmosphere, such as silane gas SiH<sub>4</sub>, prior to formation of the polysilicon layer 30 to thereby reduce the oxygen content of the tungsten nitride layer 28 and reduce the thickness of any silicon dioxide layer 36 thereafter formed.

In another embodiment of the present invention discussed with reference to Figure 6, a first conductive layer such as a tungsten nitride layer 128 is deposited over a substrate 122 and a dielectric layer 126, such as a tantalum pentoxide layer, is deposited over the tungsten nitride layer. In this situation, the deposition of the tantalum pentoxide layer 126 may cause the tungsten nitride layer 128 to incorporate oxygen, reducing the capacitance of a capacitor including the tungsten nitride layer and tantalum pentoxide layer. Accordingly, in this embodiment of the invention, the tungsten nitride layer 128 is exposed to a N<sub>2</sub> and H<sub>2</sub> plasma or other oxygen-inhibiting agent before depositing the tantalum pentoxide layer 126. As previously described, the N<sub>2</sub> and H<sub>2</sub> plasma passivates the tungsten nitride layer 128 to thereby prevent oxygen from being incorporated within the tungsten nitride layer.

The Narwankar patent discloses a method of forming a metal oxide dielectric film having a high dielectric constant for a metal insulator silicon capacitor. Figure 2a illustrates a substrate 200 including an epitaxial substrate 201 having a doped region 202 and a patterned interlayer dielectric 204. A bottom polysilicon capacitor electrode 206 is formed in contact with the doped region 202 and over the interlayer dielectric 204. In a first step, which corresponds to block 102 in flowchart 100 of Figure 1, the substrate 200 is nitridated to form a thin silicon nitride barrier layer 205 on the bottom electrode 206 as illustrated. Narwankar states the purpose

of the silicon nitride barrier layer 205 is to form an oxidation prevention barrier layer on the bottom polysilicon capacitor electrode 206 to prevent oxygen from penetrating grain boundaries of the electrode. See column 4, lines 38-47. The silicon nitride barrier layer 205 may be formed by exposing the substrate 200 to ammonia gas NH<sub>3</sub> or, alternatively, by exposing the substrate to highly reactive nitrogen atoms formed by disassociating NH<sub>3</sub> or N<sub>2</sub> gas with microwaves. See column 4 lines 58-67 and column 5, lines 1-12. The silicon nitride barrier layer 205 is then annealed in a forming gas N<sub>2</sub>/H<sub>2</sub> ambient to form a high quality annealed silicon nitride layer 209 as shown in Figure 2b. As described in column 5, lines 53-61, other hydrogen containing ambients may be utilized to anneal the silicon nitride barrier layer 205, such as hydrogen H<sub>2</sub>, or H<sub>2</sub> and argon Ar, or H<sub>2</sub> and helium He. Figures 2c-e illustrate the substrate 200 during various steps of the formation of the metal insulator silicon capacitor, and Figure 1 illustrates a flowchart depicting the process of fabricating the capacitor.

Narwankar neither discloses nor suggests treating the bottom polysilicon capacitor electrode 206 in an N<sub>2</sub>/H<sub>2</sub>, N<sub>2</sub>, or NH<sub>3</sub> plasma. As described in column 5, lines 38-52, by heating and exposing the substrate 200 to hydrogen and nitrogen gases, defects such as pinholes in the silicon nitride film 205 are eliminated or substantially reduced to prevent oxygen from penetrating through the silicon nitride barrier layer and oxidizing the polysilicon electrode 206. In contrast, in the present invention the tungsten nitride layer 52 or other conductive layer is exposed to an N<sub>2</sub>/H<sub>2</sub>, N<sub>2</sub>, and NH<sub>3</sub> plasma having ions of a specific energy to more precisely passivate the conductive layer as desired. Thus, no subsequent annealing is required. Narwankar only suggests exposing the conductive layer to hydrogen containing gases, with inherent defects being later repaired via annealing. Narwankar does not disclose treating a conductive layer in an N<sub>2</sub>/H<sub>2</sub>, N<sub>2</sub>, and NH<sub>3</sub> plasma to thereby passivate the layer. Furthermore, Narwankar expressly states each annealing ambient must contain hydrogen (column 5, lines 53-61), and thus teaches away from the use of the nitrogen N<sub>2</sub> plasma and the CF<sub>4</sub>, HCl, and BCl<sub>3</sub> gases.

Amended claim 43 recites a method of passivating a multiplayer conductive structure including layering a first conductive material, introducing a selection of N2/H2, N2, and NH3 plasma to the first conductive material, releasing nitrogen from the plasma with electromagnetic energy, and layering a second conductive material over the first conductive material. Narwankar neither discloses nor suggests passivating the first conductive material with

an  $N_2/H_2$ ,  $N_2$ , or  $NH_3$  plasma and releasing nitrogen from the plasma with electromagnetic energy. The combination of elements recited in claim 43 is therefore allowable, and dependent claim 44 is allowable for at least the same reasons as claim 43.

Amended claim 76 recites a method of passivating a multilayer conductive structure including layering a first conductive material, introducing N<sub>2</sub> plasma to the first conductive material, releasing nitrogen from the plasma with electromagnetic energy, and layering a second conductive material over the first conductive material.k Once again, Narwankar neither discloses nor suggests passivating the first conductive material in an N<sub>2</sub> plasma and releasing nitrogen from the plasma with electromagnetic energy. The combination of elements recited in claim 76 is therefore allowable.

Amended claim 77 recites a method of passivating a multilayer conductive structure including layering a first conductive material, introducing an NH<sub>3</sub> plasma to the first conductive material, releasing nitrogen from the plasma with electromagnetic energy, and layering a second conductive material over said first conductive material. Narwankar neither discloses nor suggests passivating the first conductive material in an NH<sub>3</sub> plasma and releasing nitrogen from the plasma with electromagnetic energy. The combination of elements recited in claim 76 is therefore allowable.

New claim 78 recites a method of passivating a multiplayer conductive structure including layering a first conductive material, introducing a selection of CF4, HCl, and BCl3 gases to the first conductive material, and layering a second conductive material over the first conductive material. As previously mentioned, Narwankar neither discloses nor suggests introducing a selection of CF4, HCl, and BCl3 gases to the first conductive material. The combination of elements recited in claim 78 is therefore allowable.

All pending claims are in condition for allowance, and favorable consideration and a Notice of Allowance are respectfully requested. The Examiner is requested to contact the undersigned at the number listed below for a telephone interview if, upon consideration of this amendment, the Examiner determines any pending claims are not in condition for allowance.

Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached page is captioned "Version with Markings to Show Changes Made."

Respectfully submitte

Registration No. 42,118

PFR:asw

Enclosures:

Postcard

Check

Fee Transmittal Sheet (+ copy)

Request for Continued Examination (+ copy)

Revocation and Substitute Power of Attorney

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## VERSION WITH MARKINGS TO SHOW CHANGES MADE

## In the claims:

Claims 43, 44, 76 and 77 have been amended as follows:

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43. (Amended) A method of passivating a <u>multiplayer</u> conductive structure, comprising:

layering a first conductive material;

introducing a selection of N2/H2, N2, and NH3 plasma [gas] to said

first conductive material;

releasing nitrogen from said [gas] plasma with electromagnetic

energy; and

layering a second conductive material over said first conductive

material.

44. (Amended) The method in claim 43, wherein said step of releasing nitrogen from said [gas] plasma with electromagnetic energy comprises directing ultraviolet light toward said gas.

76. (Amended) A method of passivating a multilayer conductive structure, comprising:

layering a first conductive material;

introducing N2 [gas] plasma to said first conductive material;

releasing nitrogen from said [gas] plasma with electromagnetic

energy; and

layering a second conductive material over said first conductive

material.

77. (Amended) A method of passivating a multilayer conductive structure, comprising:

layering a first conductive material;

introducing NH<sub>3</sub> [gas] <u>plasma</u> to said first conductive material; releasing nitrogen from said [gas] <u>plasma</u> with electromagnetic

energy; and

layering a second conductive material over said first conductive

material.

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